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(54) Title of the Invention: **Ink Composition For Coating Flexible Circuit Substrate**

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SPECIFICATION

1. Title of the Invention

Ink Composition for Coating Flexible Circuit Substrate

2. Claims

(1) A solvent-free, one-component ink composition for coating a flexible circuit substrate, characterized in comprising as main components:

(a) a heat-curable, flexible epoxy resin that is liquid at normal temperature;

(b) a latent curing agent for epoxy resins;

(c) a mixture of a crosslinked vinyl monomer and an ultraviolet-crosslinkable unsaturated prepolymer containing two or more terminal ethylene groups; and

(d) a sensitizer for initiating crosslinking of the prepolymer with the vinyl monomer by active light.

(2) The ink composition for coating a flexible circuit substrate according to claim (1), comprising as a main component a component in which components (c) and (d) are added in a mixing ratio of 20 to 200 weight parts with respect to 100 weight parts of components (a) and (b).

(3) The ink composition for coating a flexible circuit substrate according to claim (1) or (2), wherein the heat-curable, flexible epoxy resin that is liquid at normal temperature is a urethane-modified epoxy resin.

(4) The ink composition for coating a flexible circuit substrate according to claim (1) or (2), wherein the heat-curable, flexible epoxy resin that is liquid at normal temperature is a diglycidyl ether resin with bisphenol A side chains.

(5) The ink composition for coating a flexible circuit substrate according to claim (1), (2), (3), or (4), wherein the latent curing agent for epoxy resins is one or more types selected from the group that includes BF_3 -amine complexes, dicyandiamide complexes, and imidazole curing agents.

(6) The ink composition for coating a flexible circuit substrate according to claim (1), (2), (3), (4), or (5), wherein the unsaturated prepolymer is a so-called epoxy acrylate, which is a product of reacting a bisphenol A-epichlorohydrin epoxy resin prepolymer with acrylic acid or methacrylic acid.

(7) The ink composition for coating a flexible circuit substrate according to claim (1), (2), (3), (4), (5), or (6), wherein the sensitizer is a benzoin compound.

3. Detailed Description of the Invention

The present invention relates to a developable, one-component, solvent-free ink composition for coating a flexible circuit substrate.

Various types of inks are commercially available for the purpose of coating the surfaces of hard circuit substrates, and applications thereof include so-called etching resists used for etching, plating resists used for plating, solder resists used for soldering, cover coatings for circuit protection, and other applications. Major applications include (1) so-called heat-curable inks whose method of use involves admixing curing agents, fillers, pigments, solvents, and the like into an alkyd-melamine, epoxy resin, or other so-called heat-curable resin to form an ink by

the usual method, screen printing the ink onto a circuit substrate, and forming a heat-cured coating by drying and heating the product; (2) optically crosslinked inks mainly composed of polyvinyl cinnamates to which optical developability is imparted by adding a sensitizer, wherein the inks are applied to a circuit substrate and dried to vaporize the solvent, the coated substrate is exposed through a mask, the product is developed, and the unexposed or exposed portions are removed to form an image; and (3) ultraviolet-curable inks and the like whose main component is an acrylate prepolymer, an acrylate monomer, and an ultraviolet sensitizer.

However, almost all of these and other inks are for use with hard circuit boards, and coating inks for flexible circuit substrates, which have recently seen a sharp increase in demand, are almost nonexistent or are extremely inadequate, due in part to strict requirements for their performance. Specific features of the required performance include the following.

(1) The substrate base film is flexible, so a high degree of flexibility is also required for the coating layer itself. Soldering and other hot processing steps are also performed, so there must be no reduction in flexibility after such high-temperature processing. Among the presently few commercially available products, alkyd melamines and common bisphenol A-type epoxy coating agents have drawbacks in this area of performance.

(2) A flexible thick coating is required to enhance reliability. In this regard, all inks other than ultraviolet-curing inks contain a solvent, and, as is widely known, the solvent cannot be completely removed in the drying step when thick coating is performed, so the thickness of a coating film is inherently limited.

(3) Strong adherence or adhesion to the circuit substrate is required. Regarding this requirement, solvent-containing heat-cured inks mainly composed of alkyd melamines, epoxy resins, and the like have high adherence or adhesion, but optically crosslinked inks mainly composed of polyvinyl cinnamates, and ultraviolet-cured inks mainly composed of an acrylate prepolymer and an acrylate monomer are crosslinked by a curing mechanism that uses the so-called radical reaction involving vinyl groups, and this reaction is known to have extremely severe curing contraction, so adequate adherence or adhesion to the circuit substrate is difficult to obtain. Consequently, optically crosslinked inks are presently used only as etching resists for their high development performance, since they do not withstand use as coating agents when

harsh conditions are required, and ultraviolet-crosslinked inks are used only as simple covering films that do not undergo any post-processing that takes advantage of their high-speed curing properties.

(4) High thermal resistance and solvent resistance are required. These properties include the thermal resistance exhibited in the hot processing step during soldering that follows coating, and the solvent resistance exhibited during plating that follows coating, and although heat-cured inks are relatively good in these aspects, they are inherently hard resins, so flexibility after heat treatment cannot be obtained, and thermal resistance is all but nonexistent as regards flexible circuit boards. Thus, coatings obtained using optically crosslinked and ultraviolet crosslinked inks have weak adhesion to the substrate, and the abovementioned requirements cannot be met.

(5) Workability during application or printing is required at the same time as is coating precision, and coatings obtained using a heat-cured screen therefore have poor precision.

(6) Other requirements include high electrical performance, requirements for the operating environment, and the like.

There is a strong need in the industry for inks that can be used for flexible circuit boards and that combine the advantages of heat-cured coating inks with the advantages of light or ultraviolet crosslinked inks in addition to being pliable.

Proposals such as the one described in JP (Kokai) No. S50-14431 have been made to address such requirements. Specifically, a photosensitive resin composition is proposed that is made up of (a) a photopolymerizable unsaturated compound containing two terminal ethylene groups; (b) a photoreactive linear polymer compound containing tetrahydrofurfuryl groups in its side chains or terminals; (c) a sensitizer for initiating polymerization of an unsaturated compound by exposure to active light; and (d) a curing agent for epoxy resins. This composition is designed by a method in which the excellent characteristics of adherence, thermal resistance, and solvent resistance observed in heat-cured epoxy resins are combined in an optimal manner with the developability characteristic possessed by light- or ultraviolet-cured resins. The aforementioned invention also imparts film thickening properties by adding a linear polymer compound having optical crosslinking properties and containing a tetrahydrofurfuryl group, and

is furthermore aimed at obtaining a film coating. However, it has become clear as a result of investigation that the above proposal is aimed at a multipurpose coating agent that does not incorporate the idea of application to flexible circuit boards indicated in the description of the present invention; that the addition of a film-forming component absolutely presupposes the use of a solvent; and that although it is possible to obviate the use of a solvent if the product is converted to a dry film, a large quantity of a linear polymer must be added to obtain a film, so the characteristics of the epoxy resin component are adversely affected, heat becomes necessary to evaporate the solvent during film formation, and reaction of the acrylate monomer with the amine epoxy curing agent is unavoidable, resulting in secondary problems such as impaired light- or ultraviolet crosslinking, reduced curing performance of epoxy resins during post-heating, and reduced shelf performance.

Specifically, various drawbacks occur due to the presence of a solvent, and when coating is performed by lamination after a film is formed, adherence inevitably suffers in comparison to a product in which the solvent is vaporized from the ink. When the object is to obtain adequate adherence, thermal resistance, solvent resistance, and other properties, it is impossible to avoid using a large quantity of polyfunctional acrylate monomers because of the need to maximize the crosslinking density, or to prevent the resulting coating from becoming a hard film because of the need to maximize the crosslinking density of the epoxy resin. All this results in a product unsuitable as a coating layer for a flexible circuit board.

Unsatisfied with this state of affairs, the inventors conducted various investigations of a coating ink composition for a flexible circuit substrate aimed at achieving such objects as the following. Specifically, the present invention provides:

- (1) a solvent-free, one-component ink composition;
- (2) a composition that can be developed by exposure to ultraviolet rays;
- (3) a composition whereby a flexible coating film is obtained;
- (4) a composition whereby a coating film is obtained having adhesion, thermal resistance, and chemical resistance by heat treatment;
- (5) a composition that enables thick coating;
- (6) economic efficiency;

(7) excellent electrical performance, and the like.

As a result, it was discovered that all of these conditions are satisfied by an ink composition that is mainly composed of a resin component made up of a liquid flexible epoxy resin, a latent curing agent, an ultraviolet crosslinkable unsaturated prepolymer having two or more terminal ethylene groups, and a crosslinked vinyl monomer to which a sensitizer is added at normal temperature, and the present invention was thus developed. Specifically, a developable epoxy resin ink composition was discovered. The breakthrough discovery was made that whereas a heat-cured article of epoxy resin containing an unexposed unsaturated prepolymer and an unreacted crosslinked vinyl monomer can be dissolved and dispersed in a developing solution insofar as significant curing does not take place, a heat-cured article composed of an epoxy resin containing an exposed crosslinked material can be rendered insoluble in the developing solution merely by advancing curing to a small degree, and skillful utilization of this effect led to the discovery of the present composition.

Details of the present invention will be described hereinafter.

The ink composition for coating a flexible circuit substrate of the present invention must contain, among various types of epoxy resins, a liquid flexible epoxy resin that is liquid at normal temperature. So-called urethane-modified epoxy resins, diglycidyl ethers of bisphenol A-alkylene oxide adducts, and so-called diglycidyl ethers with bisphenol A side chains are appropriate, and dimer acid diglycidyl esters, polyalkylene glycol diglycidyl ethers, aliphatic diglycidyl ethers, diglycidyl ethers of alkyl phenol derivatives, and the like may also be used as needed.

The essential components of the present invention must include a so-called latent curing agent among curing agents for epoxy resins so that the composition can be made into a one-component product. So-called boron trifluoride complexes are preferred, and a boron trifluoride monoethylamine complex is particularly suitable among these. With this type of curing agent for epoxy resins, flexible epoxy resins that normally cure at a low rate can be cured at a rate not significantly different from that of a so-called common bisphenol A-type epoxy resin, and this type of curing agent also has the characteristic of excellent workability due to its so-called latency, which is a property whereby the agent does not react below a certain temperature. Other

dicyandiamide and imidazole-type curing agents can also be used as needed. The added quantities thereof can be 1 to 10 weight parts per 100 weight parts of the epoxy resin.

The composition must contain as a third essential component a crosslinked vinyl monomer and an ultraviolet-crosslinkable prepolymer containing two or more terminal ethylene groups. The prepolymer may be a so-called epoxy acrylate, urethane acrylate, polyester acrylate, or other prepolymer that is used in common UV-cured inks and is fluid at normal temperature or is soluble in a crosslinked vinyl monomer. Epoxy acrylates are preferred when applied in the present composition. Suitable crosslinked vinyl monomers include styrene, divinyl benzene, vinyl acetate, alkyl acrylate, mono- or polyethylene glycol diacrylate, alkyl methacrylate, mono- or polyethylene glycol dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, trimethylol propane trimethacrylate, pentaerythritol diacrylate, pentaerythritol diacrylate, tetrahydrofurfuryl methacrylate, and other vinyl monomers, and trimethylol propane triacrylate is preferred for its compatibility with epoxy resin when used in the present composition. The used quantity thereof may be in the range of 20 to 200 weight parts of mixture with respect to 100 weight parts of the epoxy resin, and a relatively small addition of 40 to 60 weight parts with respect to the epoxy resin is preferred in order to maintain the performance of the epoxy resin.

Another essential component of the present invention is a sensitizer for initiating polymerization of the aforementioned prepolymer with the vinyl monomer by irradiation with active light. Appropriate sensitizers include benzophenones, Michler's ketones, benzoin alkyl ethers, and the like.

Various components may be added besides the essential components above in order to form an ink composition with the coating ink composition of the present invention. Various inorganic fillers, thixotropic agents, pigments, antifoaming agents, and the like are used according to techniques for ink manufacturing. It is unnecessary to add solvents.

With the ink composition of the present invention, a mixture obtained by adding auxiliary components to the abovementioned essential components is made into ink by the usual method using a three-roll or other ink mill, yielding a one-component ink composition having good shelf life and containing absolutely no solvents.

The ink composition of the present invention is applied to the entire surface of a substrate by screen or mask printing. The system in this case is an inorganic solvent system that does not contain a film-thickening component, and therefore is characterized in that (1) rinsing of the screen is unnecessary, (2) a thick film can be formed, (3) a drying step for removing the solvent can be dispensed with, (4) the operating environment is favorable, and the like.

UV rays are then selectively directed solely to the necessary portions through a negative mask. The ink composition containing no film-forming component according to the present invention has the drawback of being incapable of adhesive exposure, but the level of precision needed in actual practice is adequately obtained even by indirect exposure. It is possible to appropriately use a method whereby a single-layer transparent film is placed on the coating surface and direct exposure is performed, a method whereby a solution of Poval or another water-soluble polymer, or a polymer solution soluble in the developing fluid is sprayed to form a quick-drying coating film and adhesive exposure is performed, or another method.

The exposed coating is heat-cured for 5 to 60 minutes at 100°C to 150°C, and the coating thus obtained is developed using trichlene or another solvent. A point of interest here is that although the unexposed portions can be dissolved in the developing solution even when the epoxy resin is quite cured, the exposed portions are totally insoluble in the developing solution, and a highly precise image can be obtained after development. The product is thoroughly rinsed and dried after development, and a circuit substrate having a coating layer is obtained. Post-baking may also be performed if needed.

The coating layer thus obtained is resistant to heat to the extent that it can withstand being folded 180° after soldering, and possesses excellent solvent resistance whereby it cannot be attacked by strong acids, alkali aqueous solutions, aromatic hydrocarbons, ketone solvents, or halogenated hydrocarbon solvents. The coating layer has very strong adhesion to the substrate surface and is suitable for use as a soldering resist, a plating resist, a cover coating, or other permanent protective film for a flexible circuit substrate.

Working examples will be described hereinafter.

Working Example 1

Flexible epoxy resin (EPU-6, mfd. by Asahi Denka Co., Ltd.)	100 weight parts
BF ₃ monoethylamine	5 weight parts
Epoxy acrylate (Epikote acrylate 370, mfd. by Shell Co.)	35 weight parts
Trimethylol propane triacrylate	15 weight parts
Benzoin ethyl ether	1.5 weight parts
Powdered silica (Aerosil, mfd. by Japan Aerosil)	10 weight parts
Silicon antifoaming agent (SH-5540, mfd. by Toray Silicon Co.)	0.5 weight parts

An ink was made from the above components in a three-roll mill and applied in a thickness of 50 μ to a flexible circuit substrate by a common screen printing method. So-called nonadhesive exposure (indirect exposure) was then performed for one minute at an intensity of 4000 $\mu\text{W}/\text{cm}^2$ through a negative mask at a distance of 100 μ from the photosensitive surface. A 3-kW ultra high-pressure mercury lamp manufactured by Oak Manufacturing was used as the light source. The product was heated for 30 minutes at 120°C immediately after exposure, cooled, and developed by spraying for one minute using 1,1,1-trichloroethane.

An image precisely conforming to the negative mask was obtained, and no change was observed after the product was dipped for 10 minutes each in methyl ethyl ketone, acetone, chloroform, trichlene, methanol, isopropanol, toluene, benzene, xylene, and 50% sulfuric acid aqueous solution. Separation from a copper foil was also not observed.

No change was observed after dipping the product for two minutes in a solder bath at 260°C after these tests, and the product passed when folded 150 times at 0.8 mm R in the JIS P 8115 folding test conducted thereafter. It was apparent from these results that the protective coating films thus obtained were excellent as permanent protective films for a flexible circuit substrate.

Working Example 2

Bisphenol A epoxy resin with flexible side chains (EP-4000, mfd. by Asahi Denka Co., Ltd.)	100 weight parts
BF ₃ monoethylamine	2 weight parts
2-phenyl-4-methyl-5-hydroxymethylimidazole	5 weight parts
Epoxy acrylate (VR-90X, mfd. by Showa Highpolymer)	30 weight parts
Trimethylol propane triacrylate	20 weight parts
Benzoin ethyl ether	1.5 weight parts
Powdered silica (Aerosil, mfd. by Japan Aerosil)	8 weight parts
Silicon antifoaming agent (SH-5540, mfd. by Toray Silicon Co.)	0.5 weight parts

The same operations as in Working Example 1 were performed for the above mixture, and an image precisely conforming to the negative mask was obtained after development.

The product was then heated for one hour at 130°C, and a protective coating film was obtained having excellent solvent resistance, chemical resistance, adhesion, and flexibility.

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